POROSITY OF CERTAIN IRAQI NATURAL SILICA BY MERCURY POROSIMETRY MEASUREMENTS

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Abstract
A mercury porosimeter has been used to measure the intrusion volumes on three types of Iraqi natural silica which were: glass sand, standard sand, and flint clay. The intrusion volumes were used to calculate the pore diameter, pore volume, pore area, and pore size distribution. The variation of the pore area in the silica as well as of the pore volume followed the sequence:-

Flint Clay > Standard Sand > Glass Sand

The order of variation of the properties in this sequence was correlated with the order of the crystinilty of silica.

Introduction
Porous materials are being used as molecular sieve, catalysis, humidity sensors, and contaminant barriers[1-2]. In particular, recent studies[3] propose the use of microprous (pores < 2 nm) and mesopor-ous (pores 2-50 nm) minerals as adsorbents for pollutants in aqueous systems. In addition, extend-ing the range of available pore size and internal surface area is of great interest in catalytic supports, sorbents, and thermal insulation.

A Gast electromagnetic vacuum microbalance has been used in a previous work[4,5] to measure the sorption isotherms of nitrogen at 78 K on raw and intermediate materials as well as on products of the cement industries in the country. These measure-ments provided information on the sorption capacity, specific surface, and porosity of these substances. In other work[6], the specific surface and porosity of three types of zeolite molecular sieves were measured by gravimetric sorption measurements of nitrogen. The order of variation of the porosity properties was correlated with the order of variation of the molecular masses and the extent of Al_2O_3, SiO_2, and H_2O chains present in the molecular sieves.

The majority of the published data dealt with the surface area of industrial silica using point-B and BET methods[2,7-8]. Sigel et al.[9] Prepared more highly porous xerogel and has a low thermal conductivity which makes it a good thermal insulation. It has a bulk density less than about 0.7g/cm3 and has at least about 60% porosity or greater. The surface area was more than 800m2/g using BET method and the average pore diameter was 7.9 nm using the BJH method. Kim et al.[10] Prepared an ultrahigh surface area nanoporous silica particals via an sol-gel process. The surface area and pore volume of the produced nanoporous silica particals was found to increase with increasing sol-gel hydrolysis time and varies between 200 and 1200 m2/g in the pore size range of 2-10 nm. Katsuro et al.[11] Invented a method of producing a silica gel by hydrolyzing silicon alkoxide. The silica gel produced by such a method has a pore volume and a specific surface area larger than of conventional one, and the pore volume is generally frome 0.6 to 1.6 ml/g as measured by a nitrogen gas adsorption method. Further, the specific surface area is generally from 300 to 900 m2/g as measured by a BET method by nitrogen gas adsorption and has amode diameter (Dmax) of less than 20 nm on a pore distribution curve calculated by a BJH method. No data have been found in the published research on detailed pore volume, pore size, and pore surface area. Therefore, the present work is the first attempt to investigate the pore properties of three important types of Iraqi natural silica.

Experimental
The measurements were made using mercury porosimeter, model "poresizer 9320", obtained from micromeritics, USA.

The mercury porosi-meter[12,13] is a device which is capable of generating suitably high pressures and measuring simultaneously both the pressure and the volume of the mercury taken up by the pores.

The measurements was carried out as follows:

On an analytical balance the silica specimen to be examined was weighted and dried in vacuum oven at (120C) for over night. After drying process, the specimen was transfered to the low pressure chamber and the measurements proceeded automatically recording the pressure (in psia) and intrusion reading (in pF) (Pf = pico farad). The same procedure was employed after the sample was transfered to the high pressure chamber. The duration time of the experiment lasted about 5 hours.

Three samples of Iraqi natural silica have been used. These are glass sand, flint clay, and standard sand which have been obtained from state company of geological survey and mining-ministry of industry and minerals. The specification of glass sand and flint clay are presented in table (1), while the standard sand is a processed (washed and sieved) sands used for cement testing. It constitute about 10% of the total sands of Al-Hussainiyat formation and the SiO_2 content is > 98%. The samples were ground and sieved and the powder whose the partical size between 106 and 202 um has been used.

Table (1)
Chemical compositions of the two different Iraqi natural silica.

Type	Chemical Analysis								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	L.O.I
Glass Sand	96.5-98	0.5-1.6	0.3-0.5	0.1-0.2	0.1-0.4	0.1-0.2	<0.1	<0.1	--
Flint clay	38-45	35.5-41.5	0.5-1.96	1.4-3	0.2	0.1	--	--	13.4-15.1

Results and Discussion

The porosity measurements enabled the identification of pore volume, pore size, pore area, and the most abundant pores that are present in the materials. Table (2) shows typical pore size distribution data form and pore area distribution data form for glass sand.

Table (2)
Pore volume and pore area distribu-tion data form for glass sand.

Pressure psia	Pore size/ um	Intrusion reading pF	Cumulative intrusion pF	Cumulative pore volume cc/gm	Average pressure psia	Incremental pore volume cc/gm	Average pore size um	Incremental pore area m2/gm	Cumulative pore area m2/gm
0.9	200	38.07	--	--	--	--	--	--	---
2.3	78.6	36.90	1.17	0.0252	1.6	--	113	--	0.0009
3.8	47.6	29.18	8.89	0.1918	3.05	0.1666	59.3	0.0112	0.0129
4.7	38.5	27.53	10.54	0.2275	4.25	0.0357	42.5	0.0034	0.0214
5.6	32.3	26.89	11.18	0.2413	5.15	0.0138	35.1	0.0016	0.0275
6.8	26.6	26.47	11.60	0.2503	6.2	0.0090	29.2	0.0012	0.0343
7.9	22.9	26.23	11.84	0.2555	7.35	0.0052	24.6	0.0008	0.0415
10.4	17.4	25.97	12.10	0.2611	9.15	0.0056	19.8	0.0011	0.0527
11.8	15.3	25.88	12.19	0.2631	11.1	0.0020	16.3	0.0005	0.0646
12.9	14.0	25.82	12.25	0.2644	12.35	0.0013	14.6	0.0004	0.0724
13.3	13.6	25.80	12.27	0.2648	13.1	0.0004	13.8	0.0001	0.0768
304	0.59	29.45	12.27	0.2648	--	--	---	--	---
352	0.51	29.35	12.37	0.2669	328	0.0021	0.55	0.0152	1.938
410	0.44	29.20	12.52		381	0.0033	0.47	0.0278	2.280
540	0.33	29.10	12.62	0.2723	475	0.0021	0.38	0.0220	2.859
1103	0.16	28.97	12.75	0.2751	821.5	0.0028	0.22	0.0509	5.002
3175	0.06	28.60	13.12	0.2831	2139	0.0080	0.09	0.3765	13.32
4580	0.03	28.54	13.18	0.2844	3877.5	0.0013	0.05	0.1106	24.20
7200	0.02	2851	13.21	0.2851	5890	0.0007	0.03	0.0903	36.79

Calculating the pore diameter intruded by mercury at each pressure requires solving the basic equation (Washburn equation)[7,8]: $D = -4\ \gamma \cos \Theta/P$

Where

D = the pore diameter, in units of micrometer.

γ = the surface tension of mercury, 485 dynes/cm.

Θ = the contact angle between mercury and the solid containing the pores and generally varies around 130 degrees.

P = the pressure in pounds per square inch.

Converting intrusion meter readings to pore volumes requires, first, calculating cumulative changes in capacitance (initial value taken as zero). These changes in capacitance are then multiplied by the conversion factor (penetrometer constant) supplied for the penetrometer (and a units conversion factor) to give the cumulative pore volume. Cumulative pore volumes per gram of sample are obtained by dividing by the weight of the sample.

The total pore surface area obtained by assuming that all the pores are cylindrical capillaries. Then the pore surface area (A) for each diameter increment is simply related to incremental pore volume (V) and the average pore diameter (D) by the equation[8]: $A = 4V/D$.

The cumulative surface area for each point is the sum of these for all preceding points.

Table (3) summarized the experimental values of pore volume, pore area, and median pore diameter on the three different Iraqi natural silica.

Table (3)
The porosity parameter of the three different types of silica.

Type of silica	Pore Volume cc/gm	Pore Area m^2/gm	Median pore diameter; um
Glass sand	0.2859	60.19	38
Standard Sand	0.3451	98.60	0.02
Flint Clay	0.6370	7	0.08

The value of D on the distribution curve corresponding to the maximum value of ΔV/Δ D is termed the median pore diameter and also called the most abundant pore diameter.

The results of table (3) indicated that the pore area as well as pore volume of the three Iraqi natural silica varied in an order that may be arranged in sequence as:

Flint Clay > Standard Sand > Glass Sand

The pore area and pore volume of flint clay is larger than that of the standard and glass sands because the silica is as quartzite form in sands, while in flint clay as amorphous form. In addition, the increased pore volume and pore area in standard sand may be due to the washing effect of acid on the glass sand.

The differential pore size distributions were estimated from the plot ΔV/ΔD against D. ΔV and ΔD is easy to obtain by differences respectively between adjacent cumulative volume and pore diameter points on table (2). The data obtained are tabulated in table (4) and illustrated in Figs. (1-3).

Table (4)
The data of pore size distributions for the three types of silica.

Glass sand		Standard sand		Flint clay	
ΔVΔD	D	ΔVΔD	D	ΔVΔD	D
0.0031	59.3	0.0029	80.3	0.0005	86.1
0.0021	42.5	0.0061	64.6	0.0024	72.3
0.0019	35.1	0.0028	53.2	0.0017	62.3
0.0015	29.2	0.0015	45.8	0.0033	54.8
0.0011	24.6	0.0098	39.3	0.0159	47.0
0.0012	19.8	0.0028	31.2	0.0161	39.3
0.0006	16.3	0.0007	25.6	0.0041	35.4
0.0008	14.6	0.0010	22.9	0.0062	32.6
0.00003	13.8	0.0012	19.0	0.0143	29.2
0.0429	0.47	0.0006	15.9	0.0038	26.0
0.0226	0.38	0.0006	14.6	0.0093	23.5
0.0174	0.22	0.0007	14.0	0.0036	20.4
0.0592	0.09	0.0005	13.6	0.0009	18.1
0.0342	0.05	0.0010	13.4	0.0027	16.5
0.0438	0.03	0.0052	0.41	0.0016	15.1
0.0667	0.02	0.0018	0.20	0.0027	14.1
		0.0842	0.09	0.0003	13.4
		0.0136	0.05	0.0776	0.42
		0.1438	0.04	0.2649	0.24
		0.3829	0.03	0.5285	0.13
		0.1283	0.02	0.5973	0.09
		0.3825	0.02	1.0730	0.08
		0.3200	0.02	0.1481	0.06
				0.0096	0.04
				0.0350	0.02

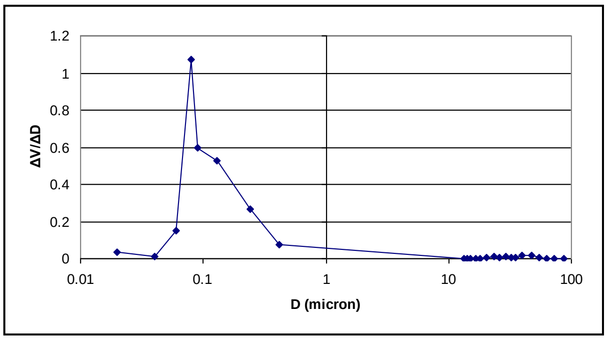

Fig. (1): Pore volume distribution over pore diameter for glass sand.

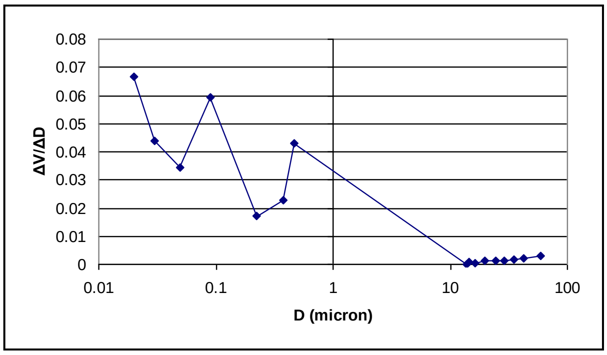

Fig. (2): Pore volume distribution over pore diameter for flint clay.

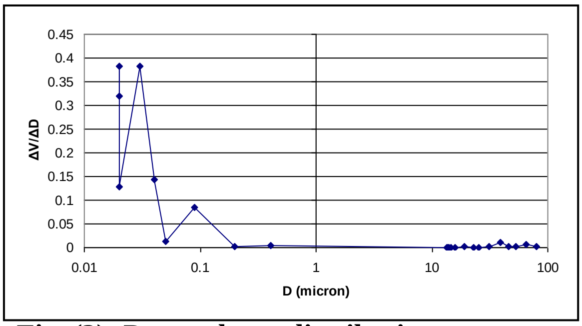

Fig. (3): Pore volume distribution over pore diameter for standard sand.

The results of fig.(1) to fig.(3) indicate the followings:

1. The pore sizes of the glass sand are greater than standard sand and flint clay. This is in agreement with the experimental pore area.
2. Flint clay exhibits the most monodisperse pore size distribution with peak at pore diameter (80 nm).
3. The standard sand has a lower pore diameter in contract with glass sand but has a greater pore volume and pore area.
4. The mesopores (defined as 2-50 nm in diameter) are exist in standard sand, while the macropores (pore diameter > 50 nm) exist in glass sand.

Conclusions

The conclusions that can be drawn from the foregoing results and discussions may be formulat-ed as in the following:

1. The variation of the pore area and pore volume in the sequence (Flint Clay > Standard sand > Glass Sand) was correlated with the order of the crysttinility of silica.
2. Flint clay exhibits the most monodisperse pore size distribution with peak at pore diameter (80 nm).
3. The mesopores are exist in standard sand, while the macropores exist in glass sand.

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الخلاصة

استخدم مقياس المسامية الزئبقي في قياس حجم الزئبق النافذ لثلاثة أنواع من السليكا الطبيعية العراقية هي: رمل الزجاج والرمل القياسي والطين الحراري. واستخدم هذا الحجم لحساب قطر وحجم ومساحة المسام بالإضافة إلى أيجاد توزيع أحجام المسام. وقد وجد أن مساحة المسام وكذلك حجم المسام لأنواع السليكا الثلاثة يتبع التسلسل الأتي: الرمل الحراري > الرمل القياسي > رمل الزجاج.

إن هذا التسلسل في تغير مساحة المسام وحجمها يتناسب مع درجة البلورية لنماذج السليكا المستخدمة.